Removal of sulfur compounds from hydrocarbon-containing gases

The present invention relates to a method of removing sulfur
5 compounds from hydrocarbon-containing gases over
copper-containing catalysts.

Hydrocarbon-containing gases such as natural gas generally
contain sulfur compounds or have to be admixed with
10 unpleasant-smelling sulfur compounds for safety reasons. On an
industrial scale, natural gas is, for example, desulfurized by
hydrogenation. However, this is not possible for every
application.

15 EP-A-1 121 922 discloses the adsorptive removal of
sulfur-containing organic components such as sulfides, mercaptans
and thiophenes from natural gas by means of silver-doped zeolites
at room temperature. A disadvantage is the high silver content.

20 It is known from BWK 54 (2002) No. 9, pages 62 to 68, that a
simple solution for the removal from natural gas of all sulfur
components which interfere in use in the fuel cell sector.

It is an object of the present invention to remedy the
25 abovementioned disadvantages and, in particular, to allow the use
of hydrocarbon-containing gases contaminated with sulfur
compounds for fuel cells.

We have found that this object is achieved by a new and improved
30 method of removing sulfur compounds from hydrocarbon-containing
gases, wherein copper-containing catalysts are used at from -50
to 150°C and a pressure of from 0.1 to 10 bar.

The method can be carried out as follows:
35
The hydrocarbon-containing gas contaminated by sulfur compounds
can be passed over a copper-containing catalyst according to the
present invention at from -50 to +150°C, preferably from -20 to
80°C, particularly preferably from 0 to 50°C, in particular from
40 15 to 40°C, very particularly preferably at room temperature, and
a pressure of from 0.1 to 10 bar, preferably from 0.5 to 5 bar,
particularly preferably from 0.8 to 1.5 bar, in particular at
atmospheric pressure.

45 Examples of hydrocarbon-containing gases which are contaminated
with sulfur compounds and can be treated by the method of the
present invention are natural gas, town gas and liquefied

petroleum gas (LPG), preferably natural gas and town gas, particularly preferably natural gas.

The contaminating sulfur compounds are generally COS, H_2S, CS_2 and
5 mercaptans and disulfides and unpleasant-smelling sulfur compounds such as tetrahydrothiophene, ethyl mercaptan, n-butyl mercaptan, t-butyl mercaptan or mixtures thereof which are added commercially for safety reasons.

10 Suitable copper-containing catalysts comprise, preferably consist of, from 30 to 99.8% by weight, preferably from 40 to 85% by weight, particularly preferably from 50 to 75% by weight, of copper oxide and from 0.2 to 70% by weight, preferably from 15 to 60% by weight, particularly preferably from 25 to 50% by weight,
15 of oxides which are selected from the group consisting of oxides of elements of groups IIB, IIIB, IVB, VIB, VIII, IIIA, and IVA of the Periodic Table of the Elements and are solids up to at least 250°C, for example oxides of zinc, scandium, yttrium, lanthanum, titanium, zirconium, chromium, molybdenum, tungsten, iron,
20 cobalt, nickel, boron, aluminum, gallium, silicon, germanium and tin, preferably those of zinc, lanthanum, titanium, zirconium, chromium, molybdenum, iron, cobalt, nickel, aluminum and silicon, particularly preferably those of zinc, lanthanum, titanium, zirconium, nickel, aluminum and silicon. The copper in these
25 "copper-containing catalysts" can be present in any oxidation state, e.g. in the oxidation state +1 or +2 or in elemental form (oxidation state = 0) or a mixture thereof, preferably in the oxidation state +2 or in elemental form or a mixture thereof, particularly preferably in the oxidation state +2.
30
The copper-containing catalysts can be prepared by generally known methods, for example by precipitation, impregnation, mixing, sintering, spraying, spray drying, ion exchange or electroless deposition, preferably by precipitation,
35 impregnation, mixing, sintering or spray drying, particularly preferably by precipitation or impregnation, in particular by precipitation.

The pulverulent copper-containing catalysts generally obtained by
40 precipitation can, if desired, be admixed with pore formers such as cellulose, glycerol, urea, ammonium carbonate, ammonium nitrate, melamine, carbon fibers or mixtures thereof after the precipitation and then be tableted, extruded or brought into any shape together with customary auxiliaries such as binders, for
45 example formic acid, polyvinylpyrrolidone (PVP), polysalicic acid or mixtures thereof, and, if desired, lubricants such as graphite, stearic acid, molybdenum sulfide or mixtures thereof

and subsequently, if desired, converted into crushed material. The copper-containing catalysts prepared by impregnation can be treated in this way either before or after impregnation.

5 The copper in the copper-containing catalysts can be partially or completely reduced to metallic copper at from 150 to 250°C, for example in the presence of hydrogen, carbon monoxide, dinitrogen monoxide or a mixture thereof or in a reducing gas atmosphere in general, either before or after shaping.
10
When used in connection with a fuel cell system, the method of the present invention can generally be employed upstream, i.e. the hydrocarbon-containing gas is purified by the method of the present invention and is then used for producing hydrogen which
15 is fed to the fuel cell. In such a case, the method of the present invention is generally suitable for all known types of fuel cells, e.g. PEM fuel cells, DMFC fuel cells (carbonate melt) and high-temperature fuel cells (GOFCs).

20 When the method of the present invention is employed in connection with a fuel cell, it is advantageous not to regenerate the exhaustive catalyst directly in the system but instead to replace it and regenerate it separately after removal from the system. This is particularly advantageous for low-power fuel
25 cells.

The method of the present invention is suitable for use in nonmobile applications, for example in fuel cell systems for the simultaneous generation of electricity and heat (e.g. block-type
30 thermal power stations), preferably in domestic power supply, and in mobile applications, for example in motor vehicles as auxiliary power units for goods vehicles, railways and passenger cars, preferably in passenger cars and goods vehicles, particularly preferably passenger cars.
35
Examples

Preparation of catalysts

40 Example 1
Preparation of a Cu-Zn-Al catalyst having the composition 52.5% by weight of CuO; 30% by weight of ZnO and 17.5% by weight of Al_2O_3

45 A mixture of a nitric acid solution of 420 g of copper(II) oxide, a nitric acid solution of 240 g of zinc oxide and a nitric acid solution of 140 g of aluminum nitrate nonahydrate was

precipitated at a pH of about 6 in an initial charge of water at 50°C by means of a solution of 474 g of sodium carbonate in 2 liters of demineralized water and the mixture was stirred for another 3 hours. The precipitate was separated off, washed with
5   water to remove sodium and nitrate ions, dried at 120°C and calcined at 400°C for 1 hour. This gave 272 g of a mixed oxide which was admixed with 1% by weight of graphite and compacted to form 20 mm pellets, pressed mechanically through a <1.6 mm screen, once again admixed with 2% by weight of graphite and
10 pressed to form pellets having dimensions of 5 x 3 mm (diameter x height).

The lateral compressive strength of the pellets was 66 N.

15 Example 2
Preparation of a Cu-Zn-Al catalyst having the composition 40% by weight of CuO; 40% by weight of ZnO and 20% by weight of Al_2O_3

Using a method analogous to Example 1, a mixture of a nitric acid
20 solution of 120 g of copper(II) oxide, a nitric acid solution of 120 g of zinc oxide and 60 g of dispersed aluminum oxie (Pural® SFC from SASOL) was precipitated at a pH of about 6.5 by means of a solution of 474 g of sodium carbonate in 2 liters of demineralized water and the mixture was worked up. The
25 calcination was carried out at 300°C for 2 hours. This gave 235 g of the mixed oxide which was converted in a manner analogous to Example 1 into pellets having a lateral compressive strength of 71 N.

30 Example 3
Preparation of a Cu-Zn-Zr catalyst having the composition 73.9% by weight of CuO; 21.1% by weight of ZnO and 5% by weight of ZrO_2

Using a method analogous to Example 1, a mixture of a nitric acid
35 solution of 370 g of copper(II) oxide, a nitric acid solution of 105.5 g of zinc oxide and a nitric acid solution of 25 g of zirconium carbonate was precipitated at a precipitation temperature of 70°C and a pH of about 6.5 by means of a solution of 474 g of sodium carbonate in 2 liters of demineralized water
40 and the mixture was worked up. The calcination was carried out at 300°C for 4 hours. This gave 540 g of a mixed oxide which was converted in a manner analogous to Example 1 into pellets having a lateral compressive strength of 66 N.

45

Example 4
Preparation of a Cu-Zn-Al-Zr catalyst having the composition 50% by weight of CuO; 30% by weight of ZnO and 17.5% by weight of Al_2O_3 and 2.5% by weight of ZrO_2

5

Using a method analogous to Example 1, a mixture of a nitric acid solution of 150 g of copper(II) oxide, a nitric acid solution of 90 g of zinc oxide, a nitric acid solution of 386.3 g of aluminum nitrate nonahydrate and a nitric acid solution of 7.5 g of

10 zirconium carbonate which had been adjusted to a pH of about 2.5 by means of sodium carbonate was precipitated at room temperature and a pH of about 8 by means of a mixture of 2 molar sodium hydroxide solution and 0.3 molar sodium carbonate solution, the mixture was maintained at 50°C for 2 hours and worked up.

15 Calcination was carried out at 600°C for 4 hours. This gave 300 g of the mixed oxide which was converted in a manner analogous to Example 1 into pellets having a lateral compressive strength of 101 N.

20 Example 5
Preparation of a Cu-Zn-Al-Zr catalyst having the composition 60% by weight of CuO; 20% by weight of ZnO, 17.5% by weight of Al_2O_3 and 2.5% by weight of ZrO_2

25 This catalyst was prepared by a method analogous to Example 4. The compressive strength of the pellets was 100 N.

Example 6
Preparation of a Cu-Zn-Al catalyst having the composition 67% by 30 weight of CuO, 26.4% by weight of ZnO and 6.6% by weight of Al_2O_3

A solution of 320 g of $Zn(NO_3)_2 \cdot 6 H_2O$ and 336.4 g of $Al(NO_3)_3 \cdot 9 H_2O$ in 600 ml of water and 2000 ml of a 20% strength by weight sodium carbonate solution were combined in such a way that the

35 precipitation occurred while stirring at 50°C and a pH of 6.7-6.9, the mixture was stirred for another 30 minutes, filtered, subsequently washed free of sodium and nitrate, dried at 120°C for 12 hours and calcined at 350°C for 2 hours.

40 The calcined ZnAl mixed oxide obtained in this way was dissolved in a nitric acid solution of copper nitrate and zinc nitrate so as to give a total atom ratio of Cu:Zn:Al = 65:25:10 and the solution was combined at 70°C and a pH of about 6.8 with 2000 ml of a 20% strength by weight sodium carbonate solution in a manner 45 analogous to the above-described precipitation procedure, the mixture was stirred for another 60 minutes, filtered,

subsequently washed free of sodium and nitrate, dried at 120°C for 16 hours and calcined at 300°C for 4 hours.

This gave 320 g of a mixed oxide which was converted in a manner analogous to Example 1 into pellets having a compressive strength of 80 N. The BET surface area was 85 m^2/g and the pore volume was 0.29 ml/g (Hg porosimetry).

Example 7

Preparation of a catalyst having the composition 65% by weight of CuO; 20% by weight of ZnO; 6% by weight of Al_2O_3; 6% by weight of ZrO_2 and 3% by weight of La_2O_3

The preparation was carried out by a method analogous to Example 2 using a nitric acid solution of 215 g of CuO, 66 g of ZnO, 145 g of $Al(NO_3)_3 \cdot 9\ H_2O$, 20 g of ZrO_2 and 10 g of La_2O_3, but the precipitation was carried out at 70°C. This gave 330 g of a mixed oxide which was converted in a manner analogous to Example 1 into pellets having a lateral compressive strength of 80 N. The BET surface areas was 109 m^2/g.

Example 8

Preparation of a catalyst having the composition 60% by weight of CuO; 20% by weight of ZnO; 10% by weight of Al_2O_3; 5% by weight of ZrO_2 and 5% by weight of MgO

The preparation was carried out by a method analogous to Example 2 using a nitric acid solution of 231 g of CuO, 77 g of ZnO, 290 g of $Al(NO_3)_3 \cdot 9\ H_2O$, 19.2 g of ZrO_2 and 19.5 g of MgO, but the precipitation was carried out at 70°C. This gave 350 g of the mixed oxide which was converted in a manner analogous to Example 1 into pellets having a lateral compressive strength of 90 N. The BET surface area was 96 m^2/g.

Example 9

Preparation of a catalyst having the composition 60% by weight of CuO; 20% by weight of ZnO; 10% by weight of Al_2O_3; 5% by weight of ZrO_2 and 5% by weight of NiO

The preparation was carried out by a method analogous to Example 2 using a nitric acid solution of 264 g of CuO, 88 g of ZnO, 323 g of $Al(NO_3)_3 \cdot 9\ H_2O$, 22 g of ZrO_2 and 22 g of NiO, but the precipitation was carried out at 70°C. This gave 400 g of the mixed oxide which was converted in a manner analogous to Example 1 into pellets having a lateral compressive strength of 80 N. The BET surface area was 114 m^2/g.

Example 10
Preparation of a catalyst having the composition
60% by weight of CuO; 20% by weight of ZnO; 10% by weight of
Al_2O_3; 5% by weight of ZrO_2 and 5% by weight of SiO_2

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The preparation was carried out by a method analogous to
Example 2 using a nitric acid solution of 200 g of CuO, 66 g of
ZnO, 241 g of $Al(NO_3)_3 \cdot 9\ H_2O$, 16.5 g of ZrO_2 and 16.5 g of SiO_2
(colloidal; Ludox™; 50% by weight in water), but the
10 precipitation was carried out at 70°C. This gave 300 g of the
mixed oxide which was converted in a manner analogous to
Example 1 into pellets having a lateral compressive strength of
90 N. The BET surface area was 125 m^2/g.

15 Example 11
Preparation of an impregnated catalyst having the composition:
14.6% by weight of CuO, 7.4% by weight of ZnO and 78% by weight
of Al_2O_3

20 1.77 kg of aluminum oxide extrudates having a diameter of 4 mm
and a water absorption of 0.557 ml/g were impregnated by covering
with an aqueous solution of 343 g of copper nitrate/liter and
156 g of zinc nitrate/liter, dried at 120°C and calcined at 520°C
for 3 hours. The impregnation procedure including drying and
25 calcination was repeated.

This gave 2100 g of the impregnated catalyst having a bulk
density of 844 g/liter, a water absorption of 0.44 ml/g and a
cutting hardness of 266 N.
30

Example 12
Preparation of an impregnated catalyst having the composition:
71.15% by weight of Al_2O_3, 18% by weight of MoO_3, 7.5% by weight
of CuO and 3.35% by weight of BaO
35

294 g of aluminum oxide extrudates in the form of 3 mm trilobes
were placed in a vessel, impregnated with 89 g of ammonium
heptamolybdate in 224 ml of water (81% strength by weight), dried
at 120°C and subsequently calcined at 370°C for 75 minutes and at
40 400°C for 135 minutes.

The extrudates were then impregnated with 155 ml of a 19%
strength by weight copper nitrate solution and subsequently dried
and calcined as before.
45

Finally, the extrudates were impregnated with 260 ml of a solution containing 230 g of barium nitrate and subsequently dried and calcined again as before.

5 This gave 405 g of the impregnated catalyst having a tapped density of 750 g/liter, a water absorption of 0.5 ml/g and a cutting hardness of 9.5 N.

Examples of use of the catalysts
10
A heatable tube reactor having a diameter of 10 mm was in each case charged with 10 g of one of the above-described catalysts in the form of crushed material (1-2 mm) and operated in a single pass. The gas leaving the reactor was passed to a gas
15 chromatograph for detection of organic carbon compounds by means of a flame ionization detector and for selective sulfur detection by means of a flame photometric detector.

After the end of the experiment, i.e. after the sulfur component
20 had broken through, the catalyst was removed from the reactor and the sulfur content was determined by standard methods (e.g. as described by Ehrenberger; "Quantitative Organische Elementaranalyse", VCH Verlagsgesellschaft, Weinheim, 1991, page 242 ff.).
25
Use example 1

The catalysts from Examples 1 to 15 were exposed to a methane stream containing 1 000 ppm of COS. The space velocity of gas,
30 i.e. the volume of gas per unit volume of catalyst and hour, was 1000 h^{-1}, and the reaction temperature was 25°C. The experiment was stopped as soon as the amount of COS in the gas leaving the reactor exceeded 1 ppm.

35 Table A summarizes the results of the sulfur content of the catalysts subsequently removed from the reactor.

Use example 2

40 The catalysts from Examples 1 to 15 were exposed to a methane stream containing 1 000 ppm of H_2S. The space velocity of gas, i.e. the volume of gas per unit volume of catalyst and hour, was 1000 h^{-1}, and the reaction temperature was 25°C. The experiment was stopped as soon as the amount of H_2S in the gas leaving the
45 reactor exceeded 1 ppm.

Table A summarizes the results of the sulfur content of the catalysts subsequently removed from the reactor.

Use example 3

5

The catalysts from Examples 1 to 15 were exposed to a methane stream containing 500 ppm of H_2S and 500 ppm of COS. The space velocity of gas, i.e. the volume of gas per unit volume of catalyst and hour, was 1000 h^{-1}, and the reaction temperature was

10 25°C. The experiment was stopped as soon as the combined amount of H_2S and COS in the gas leaving the reactor exceeded 1 ppm.

Table A summarizes the results of the sulfur content of the catalysts subsequently removed from the reactor.

15

Use example 4

The catalysts from Examples 1 to 15 were exposed to a gas stream which comprised 60% by volume of methane and 40% of propane and

20 contained 500 ppm of H_2S and 500 ppm of COS and additionally 2000 ppm of toluene. The space velocity of gas, i.e. the volume of gas per unit volume of catalyst and hour, was 1000 h^{-1}, and the reaction temperature was 25°C. The experiment was stopped as soon as the combined amount of H_2S and COS in the gas leaving the

25 reactor exceeded 1 ppm.

Table A summarizes the results of the sulfur content of the catalysts subsequently removed from the reactor.

30 It can be seen from Table A that COS and H_2S continue to be adsorbed completely on the catalyst irrespective of the presence of higher hydrocarbons. Adsorption of the higher hydrocarbons (e.g. toluene) on the catalyst was not observed.

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40

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Table A

Catalyst	Sulfur content [% by weight]			
	Use example 1	Use example 2	Use example 3	Use example 4
Example 1	8.8	8.6	8.8	8.9
Example 2	7.0	6.7	6.8	6.9
Example 3	12.3	12.0	12.1	12.0
Example 4	8.5	8.0	8.1	8.0
Example 5	9.5	9.2	9.4	9.4
Example 6	11.2	11.0	11.0	10.9
Example 7	11.2	11.0	11.2	11.2
Example 8	10.5	10.2	10.5	10.4
Example 9	10.4	10.1	10.2	10.3
Example 10	10.9	10.2	10.1	10.0
Example 11	2.5	2.1	2.3	2.25
Example 12	1.1	1.0	0.9	0.9

Use example 5

Before commencement of the experiment, the catalyst was reduced at about 200°C in a gas stream composed of about 1% by volume of hydrogen in nitrogen.

The catalysts from Examples 1 to 15 which had been reduced in this way were exposed to a methane stream containing 15 ppm by volume of tetrahydrothiophene (THT). The space velocity of gas, i.e. the volume of gas per unit volume of catalyst and hour, was 1000 h^{-1}, the reaction temperature was 25°C. The experiment was stopped as soon as the amount of THT in the gas leaving the reactor exceeded 1 ppm.

Table B summarizes the results of the adsorption capacity of the catalyst for THT up to the time at which the experiment was stopped.

Use example 6

The experiments were carried out using a method analogous to Example 5, but the catalysts were not reduced prior to commencement of the experiment.

Table B summarizes the results of the adsorption capacity of the catalyst for THT up to the time at which the experiment was stopped.

5 It can be seen from Table B that the adsorption was lower than in Use example 5 in which the catalysts were used in reduced form.

Use example 7

10 To test an optimized adsorber cartridge, the following procedure is employed: natural gas is used in place of methane. This has essentially the following composition: 84% by volume of methane, 3.5% by volume of ethane, 0.6% by volume of propane, 9.3% by volume of nitrogen, 1.6% by volume of carbon dioxide and a total
15 of about 3 500 ppm of higher hydrocarbons (C_3-C_8).

The following constituents are mixed into the natural gas: 20 ppm of COS, 20 ppm of H_2S and 15 ppm of THT.

20 The catalyst provided is in each case prereduced to an extent of 80%, so that about 80% of the catalyst bed is optimized for the absorption of THT, while the remainder is available for adsorption of COS and H_2S.

25 The space velocity of gas, i.e. the volume of gas per unit volume of catalyst and hour, is once again 1000 $l/l*h^{-1}$, and the reaction temperature is 25°C. The experiment is stopped when > 1 ppm of THT is detected for the first time in the offgas from the reactor. The adsorption capacity of the catalyst in g of THT/liter of
30 catalyst is calculated from the volume of gas passed over the catalyst up to this point in time. In all cases, neither COS nor H_2S could be detected in the offgas from the reactor up to this point in time.

35 The catalysts from Examples 1 to 15 were exposed to a methane stream containing 1 000 ppm of COS. The space velocity of gas, i.e. the volume of gas per unit volume of catalyst and hour, was 1000 h^{-1}, and the reaction temperature was 25°C. The experiment was stopped as soon as the amount of COS in the gas leaving the
40 reactor exceeded 5 ppm.

Table B summarizes the results of the adsorption capacities for sulfur-containing components.

45

Table B

Catalyst	THT adsorption capacity [g of THT per liter of catalyst]		
	Use example 5	Use example 6	Use example 7
Example 1	3.2	1.5	2.5
Example 2	2.5	1.1	2.0
Example 3	4.6	2.2	3.5
Example 4	3.1	1.6	2.5
Example 5	3.6	1.8	2.8
Example 6	4.1	1.9	3.2
Example 7	3.8	1.8	3.0
Example 8	3.6	1.8	2.8
Example 9	3.7	2.0	2.95
Example 10	3.5	1.6	2.8
Example 11	0.9	0.4	0.7
Example 12	0.3	0.1	0.2

Comparative examples

Comparative example 1

Commercial Cu-doped activated carbon (G 32-J from Süd-Chemie; containing 4.5% by weight of Cu; pore volume of 0.25 ml/g and surface area of 1000 m^2/g) as 1-2 mm crushed material was tested in a manner analogous to use example 6.

The THT adsorption capacity of this activated carbon was 0.9 g of THT per liter of activated carbon.

Comparative example 2

Commercial activated carbon (C38/4, Catalog No. 2722 from CarboTech, Essen) was tested in a manner analogous to use example 6.

The THT adsorption capacity of this activated carbon was 6.5 g of THT per liter of activated carbon.

Comparative example 3

Commercial activated carbon (Norit RB4 from Norit; pore volume = 0.13 ml/g; surface area = 1292 m^2/g) as 1-2 mm crushed material was tested in a manner analogous to use example 6.

The THT adsorption capacity of this activated carbon was 0.5 g of THT per liter of activated carbon.

Comparative example 4

5

Commercial activated carbon (Desorex K from Lurgi; pore volume = 0.55 ml/g; surface area = 1494 m^2/g) as 1-2 mm crushed material was tested in a manner analogous to use example 6.

10 The THT adsorption capacity of this activated carbon was 0.6 g of THT per liter of activated carbon.

Comparative example 5

15 Commercial Cu-doped activated carbon (G 32-J from Süd-Chemie; containing 4.5% by weight of Cu; pore volume of 0.25 ml/g and surface area of 1000 m^2/g) as 1-2 mm crushed material was tested in a manner analogous to use example 1.

20 The COS adsorption capacity of this activated carbon was 1.1 g of COS per liter of activated carbon.

Comparative example 6

25 Commercial activated carbon (Norit RB4 from Norit; pore volume = 0.13 ml/g; surface area = 1292 m^2/g) as 1-2 mm crushed material was tested in a manner analogous to use example 1.

The COS adsorption capacity of this activated carbon was 0.6 g of 30 COS per liter of activated carbon.

Comparative example 7

Commercial activated carbon (Desorex K from Lurgi; pore volume = 35 0.55 ml/g; surface area = 1494 m^2/g) as 1-2 mm crushed material was tested in a manner analogous to use example 1.

The COS adsorption capacity of this activated carbon was 0.55 g of COS per liter of activated carbon.
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